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Summer 2012

# Characterization of Polymeric Phthalocyanine Nanoparticles Using Dynamic Light Scattering Laser

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### Recommended Citation

Murarishetty, Satish Kumar, "Characterization of Polymeric Phthalocyanine Nanoparticles Using Dynamic Light Scattering Laser" (2012). *All Capstone Projects*. 49.  
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# **Characterization of polymeric phthalocyanine nanoparticles using Dynamic Light Scattering Laser**

**By**

**SATISH KUMAR MURARISHETTY**



**MASTER'S PROJECT**

Submitted in partial fulfillment of the requirements

For the Degree of Master of Science,  
With a Major in Analytical Chemistry

Governors State University  
University Park, IL 60484

2012

## **ABSTRACT**

The objective of this study is to use DLS (Dynamic Light Scattering) to analyze polymeric copper phthalocyanine nanoparticles (CuPcNPs). CuPcNPs are synthesized in order to facilitate drug penetration of bacterial biofilms for the treatment of chronic wounds. Microorganisms that reside inside the biofilms of chronic wounds are very resistant to any kind of treatment, even to the host's own immune system. Therefore we have proposed an alternative method to destroy the microorganisms existing within the biofilms. Photodynamic anti-bacterial chemotherapy (PACT) has received much attention for the past decade due to the multi-drug resistant strands. PACT uses photons, a photosensitizer, and a reactive oxygen species to eliminate both Gram+ and Gram- bacteria. In this study, the hydrophobic photosensitizer phthalocyanine has been encapsulated inside the polymeric nanoparticles and the sizes of the nanoparticles are determined using DLS technique.

## INTRODUCTION

Dynamic light scattering (DLS) is an important experimental technique in science and industry. It is also known as Photon Correlation Spectroscopy (PCS). This technique is one of the most popular methods used to determine the size of particles. The first name given to the technique was quasi-elastic light scattering (QELS) because, when photons are scattered by mobile particles, the process is quasi-elastic. QELS measurements yield information on the dynamics of the scatterer, which gave rise to the acronym DLS (dynamic light scattering)<sup>[1]</sup>. Photon correlation spectroscopy has become a powerful light-scattering technique for studying the properties of suspensions and solutions of colloids, biological solutions, macromolecules and polymers that is absolute, non-invasive and non-destructive. Technique is also useful for measuring the speed, for example for microorganisms that float in the solution, or to analyze flow in fluids. Shining a monochromatic light beam, such as a laser, onto a solution with particles in Brownian motion causes a Doppler Shift when the light hits the moving particle, changing the wavelength (typically red light at 633 nm or near-infrared at 830 nm for bimolecular applications of the incoming light. This change is related to the size of the particle<sup>[1]</sup>(Figure 1). It is possible to compute the sphere size distribution and give a description of the particle's motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function.

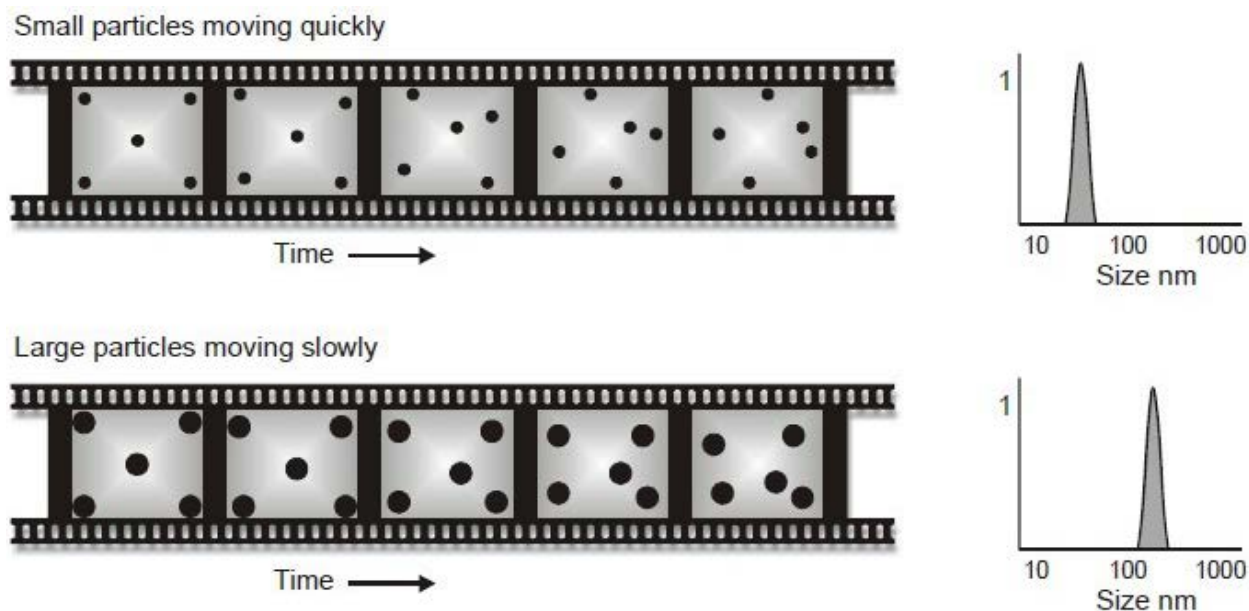


Figure: 1 Particles motion in the medium.

The particles in a liquid move about randomly and their motion speed is used to determine the size of the particle <sup>[1]</sup>.

This method has several advantages: First of all the experiment duration is short and it is almost all automatized so that for routine measurements an extensive experience is not required. Commercial "particle sizing" systems mostly operate at only one angle (90°) and use red light (675 nm). Usually in these systems the dependence on concentration is neglected. Using more sophisticated experimental equipment (projector, short wavelength light source), the methods can be not only considerably extended, but also more complicated and expensive. Simple DLS instruments that measure at a fixed angle can determine the mean particle size in a limited size range. More elaborated multi-angle instruments can determine the full particle size distribution <sup>[5]</sup>.

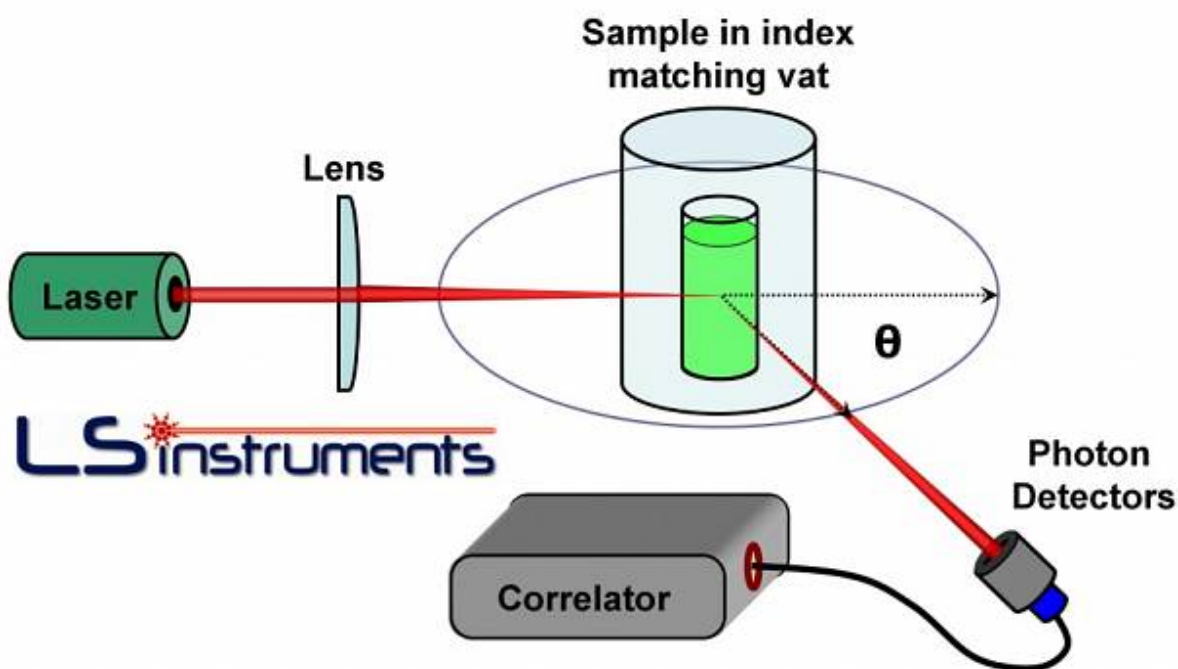


Figure 2 : Instrumentation of DLS

The principle behind dynamic light scattering is particles, emulsions and molecules in suspension undergo Brownian motion. This is the motion induced by the bombardment by solvent molecules that themselves are moving due to their thermal energy<sup>[6]</sup>.

If the particles or molecules are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles as smaller particles are “kicked” further by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein relationship.

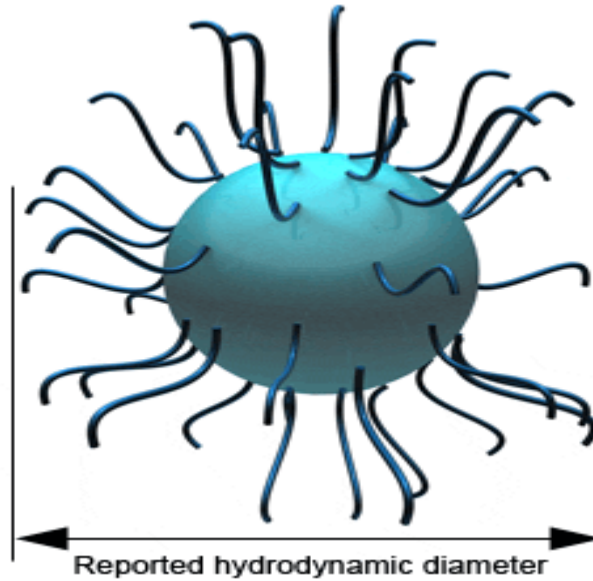


Figure 3 : Particles hydrodynamic diameter.

Brownian motion is the random motion of particles due to the bombardment by the particles suspended in within a liquid. The larger the particle, the slower the Brownian motion will be. Smaller particles are “kicked” further by the solvent molecules and move more rapidly. An accurately known temperature is necessary for DLS because knowledge of the viscosity is required (because the viscosity of a liquid is related to its temperature). The temperature also needs to be stable, otherwise convection currents in the sample will cause non-random movements that will ruin the correct interpretation of size. The velocity of the Brownian motion is defined by a property known as the translational (‘free-particle’) diffusion coefficient in infinitely-dilute solutions and is usually given as the symbol  $D_0$ . In previous section we saw, that the correlation function is an exponential decaying with time delay  $\tau$  and  $g^{[1]}(\tau)$  is the sum of all the exponential decays contained in the correlation function. It is frequently called the ‘measured intermediate scattering function’  $F(q, \tau) = \langle e^{iq \cdot \Delta r(\tau)} \rangle$  as the dynamic structure factor. According to the central limit

theorem, the probability for a particle displacement should be the Gaussian distribution function.

So we get <sup>[3]</sup>

$$F(q, \tau) = e^{-q^2 \Delta r^2(\tau)} / 6$$

Where  $(\Delta r^2(\tau))$  is the mean-square displacement of the particle in time  $\tau$  and  $q$  is the scattering vector. For a diffusing particle we have a relation<sup>[3]</sup>:  $(\Delta r^2(\tau)) = 6D_0\tau$ , and finally

$$F(q, \tau) = e^{-q^2 D_0 \tau}.$$

This relation is valid for a dilute solution of identical non-interacting spheres. According to the Einstein relation the translational self-diffusion coefficient is <sup>[3]</sup>:

$$D_0 = kBT / \zeta$$

Where  $kB$  Boltzmann's constant,  $T$  is the temperature and  $\zeta$  is the friction constant. For spherical particles we have the Stokes approximation  $\zeta = 6\pi\eta R_H$ , where  $\eta$  is the viscosity of the solvent and  $R_H$  is the particles hydrodynamic radius. Finally, the size of a particle is calculated from the translational diffusion coefficient by using the Stokes-Einstein equation:

$$R_H = kBT / 6\pi\eta D_0$$

Note that the radius that is measured in DLS is a value that refers to how a particle diffuses within a fluid so it is referred to as a hydrodynamic diameter. The radius that is obtained by this technique is the radius of a sphere that has the same translational diffusion coefficient as the particle. Factors that affect the diffusion speed of particles are discussed in the following section.

The monodisperse dilute solution,  $g^{[1]}(\tau)$  is presented by a single exponential as follows:  $g^{[1]}(\tau) = e^{-\Gamma\tau}$ . Now, we can obtain for correlation function:

$$G^{[2]}(\tau) = A(1 + \beta[e^{-2\Gamma\tau}])$$

Where  $\Gamma$  is the decay rate (the inverse of the correlation time). The decay rate is:



$$\Gamma = \tau_c^{-1} = q^2 D_0$$

The hydrodynamic diameter ( $R_H$ ), that is being reported, is the diameter or the radius of the hard sphere that diffuses at the same speed as the particle or molecule being measured. The translational diffusion coefficient will depend not only on the size of the particle “core”, but also on any surface structure, as well as the concentration and type of ions in the medium. The ions in the medium and the total ionic concentration can affect the particle diffusion speed by changing the thickness of the electric double layer called the Debye length ( $K^{-1}$ ). Any change to the surface of a particle that affects the diffusion speed will correspondingly change the apparent size of the particle. The nature of the surface and the polymer, as well as the ionic concentration of the medium can affect the polymer conformation, which in turn can change the apparent size by several nanometers.

## EXPERIMENTAL SECTION

### Formulation PACT-3A-1: ( Sample 2 )

3. Dissolve 30 mg copper Phthalocyanine (CuPc) and 4.0 mL of sulfynol- 465 in 10 mL of ethyl acetate (organic phase) over low heat with constant stirring.
- II. Dissolve 270 mg high molecular weight PEG ( $M_r > 2000$  g/mol) in 50 mL of water (water phase).
- III. Add the organic phase into the water phase while vigorously stirring until all the ethyl acetate has evaporated. Sonicate for 15 minutes.

Sample Dilution : 20 $\mu$ l of sample + 1980 $\mu$ l of water.

### Formulation PACT-3A-2: ( Sample 3 )

4. Dissolve 6 mg of copper Phthalocyanine (CuPc) and 2.0 mL of sulfynol 465 in 10 mL of ethyl acetate (organic phase) over low heat with constant stirring.
- II. Dissolve 0.2 g of poloxamer- 407 in 20 mL of water (water phase).
- III. Add organic phase into water phase while vigorously stirring over low heat until all the ethyl acetate has evaporated.
- IV. The solution is then degassed to remove the foam.
- V. Sonicate for 15 minutes.

Sample Dilution : 20µl of sample + 1980µl of water.

### **Formulation PACT-3A-3: ( Sample 1 )**

5. Dissolve 6 mg (5.5 ~~Phthalocyanine~~ Phthalocyanine (CuPc) and 2.0 mL of sulfynol- 465 in 20 mL of ethyl acetate (organic phase) over low heat with constant stirring.
- II. Dissolve 11 ~~Octadecyl~~ Octadecyl (phosphoryl)choline in 20 mL of water (water phase).
- III. Add organic phase into water phase while vigorously stirring. Keep adding water while stirring and bring the volume to 100 mL.
- IV. Keep stirring overnight until all the ethyl acetate has evaporated and bring the volume down to 20 mL.
- IV. The solution is then degassed to remove the foam.
- V. Sonicate for 15 minutes.

Sample Dilution : 20µl of sample + 1980µl of water.

### **Stabilizer and Thickening Agent**

PEG and poloxamer are well known stabilizers; therefore, no additional stabilizer is needed in some of our formulations. Carbomer, a synthetic high molecular weight polymer of acrylic acid will be used as an additional stabilizer and also as a thickening agent to increase the viscosity of all the formulations.

## RESULTS AND DISCUSSION

The particle size from DLS is derived by the autocorrelation<sup>[10]</sup> function of the sample. Initially the instrument is run with latex sample, if it works then samples should be run. Once the samples are run in DLS the effective diameter of the nanoparticle will be displayed on the monitor. We ran each sample for ten times and we calculated the mean of those readings.

**Table 1 :** Sample 1 Readings

SL.No	Diameter (nm)
1	307.1
2	328.6
3	319.4
4	311.6
5	302.6
6	305.2
7	300.2
8	308.1

9	316.9
10	324.8

Mean =  $\frac{307.1+328.6+319.4+311.6+302.6+305.2+300.2+308.1+316.9+324.8}{10} = 312.4\text{nm}$

10

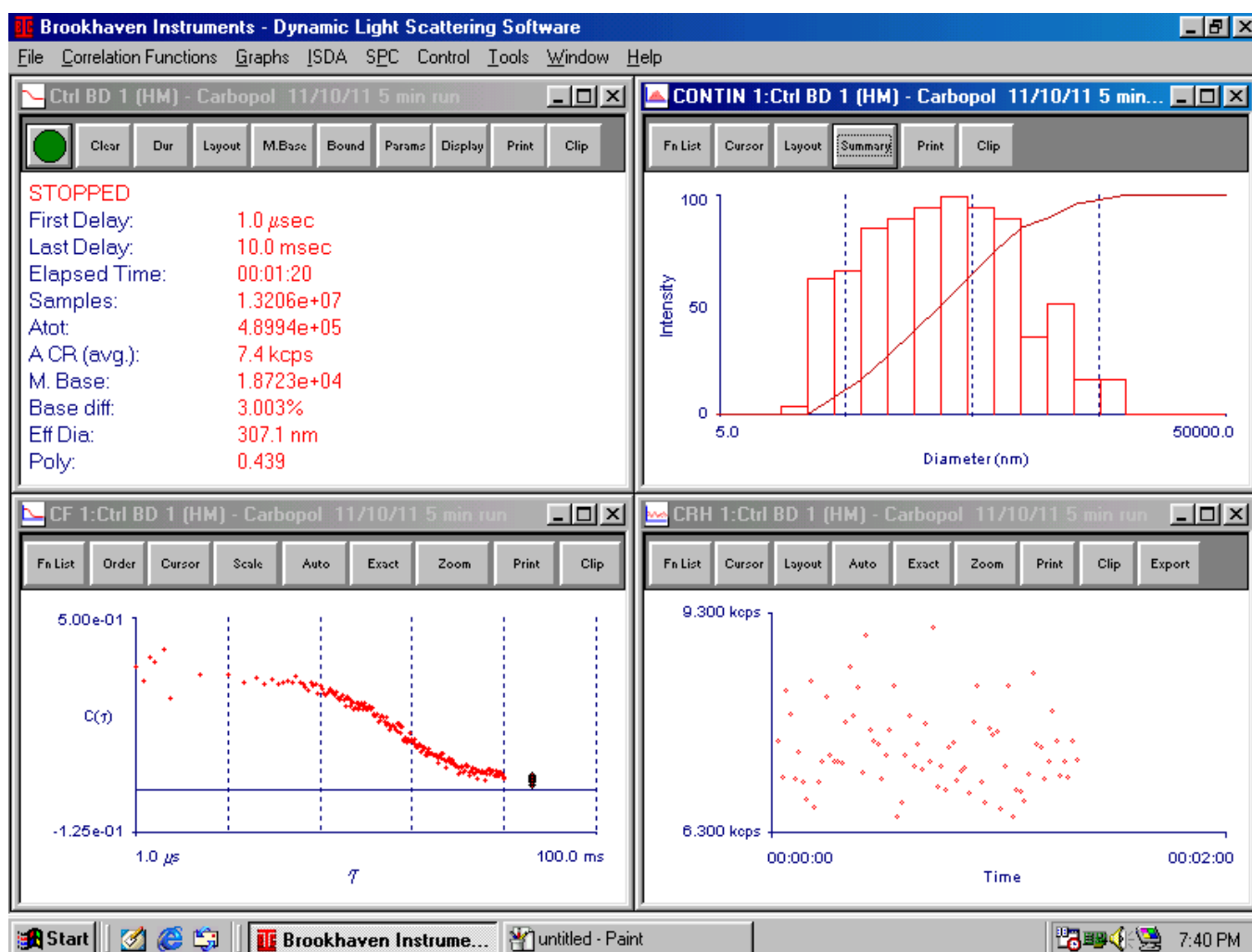


Figure 4 : DLS results of sample 1 .

**Table 2 :** Sample 2 Readings

SL.No	Diameter (nm)
1	190.5
2	188.9
3	189.5
4	199.5
5	204.1
6	195.6
7	191.2
8	195.7
9	186.7
10	191.3

$$\text{Mean} = \frac{190.5+188.9+189.5+199.5+204.1+195.6+191.2+195.7+186.7+191.3}{10} = 193.3\text{nm}$$

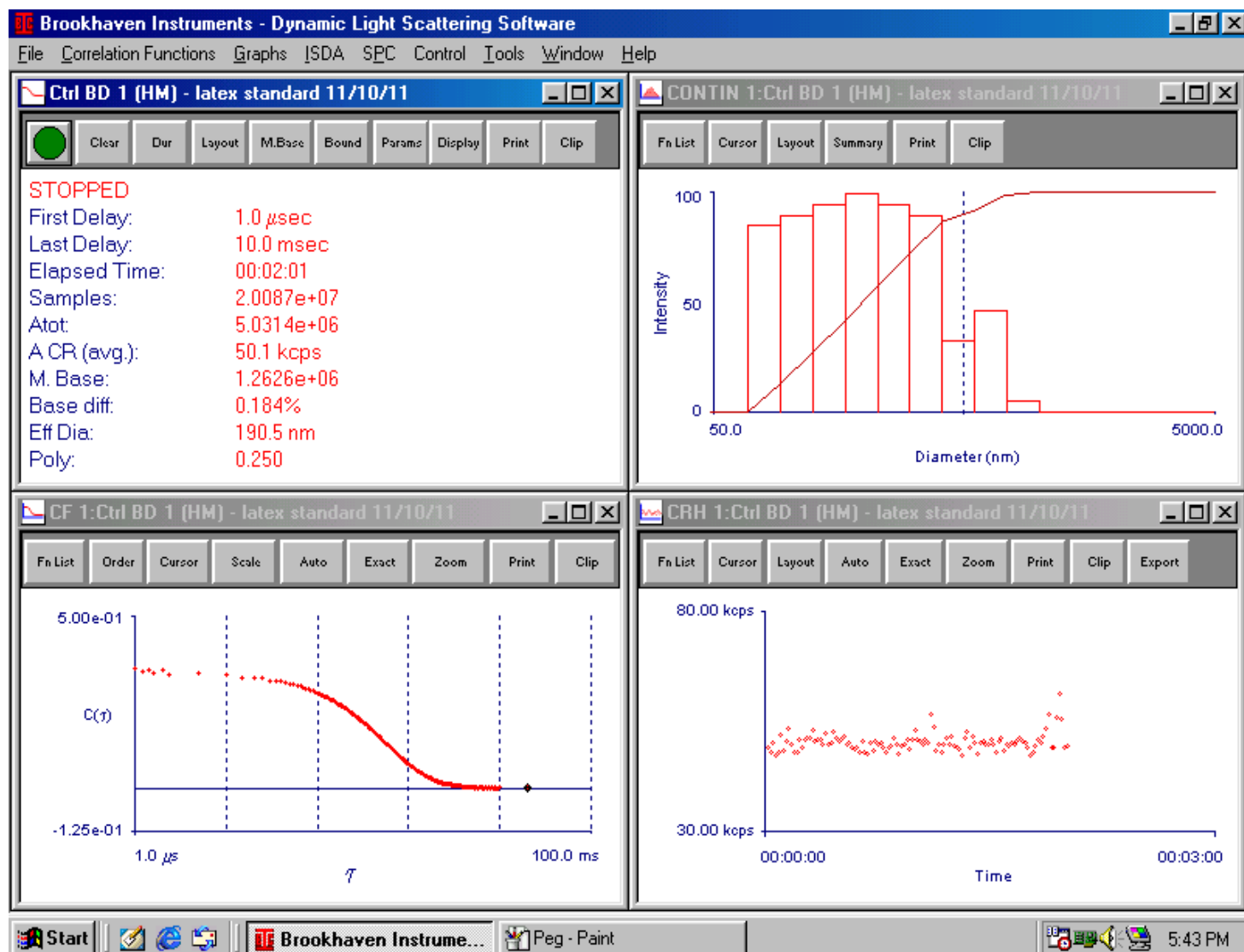


Figure 5 : DLS results of sample 2.

**Table 3 :** Sample 3 Readings

SL.No	Diameter (nm)
1	207.9
2	202.5
3	203.3
4	205.7
5	203.0
6	205.5
7	204.3
8	207.6
9	201.1
10	202.4

$$\text{Mean} = \frac{207.9+202.5+203.3+205.7+203.0+205.5+204.3+207.6+201.1+202.4}{10} = 204.33\text{nm}$$

10



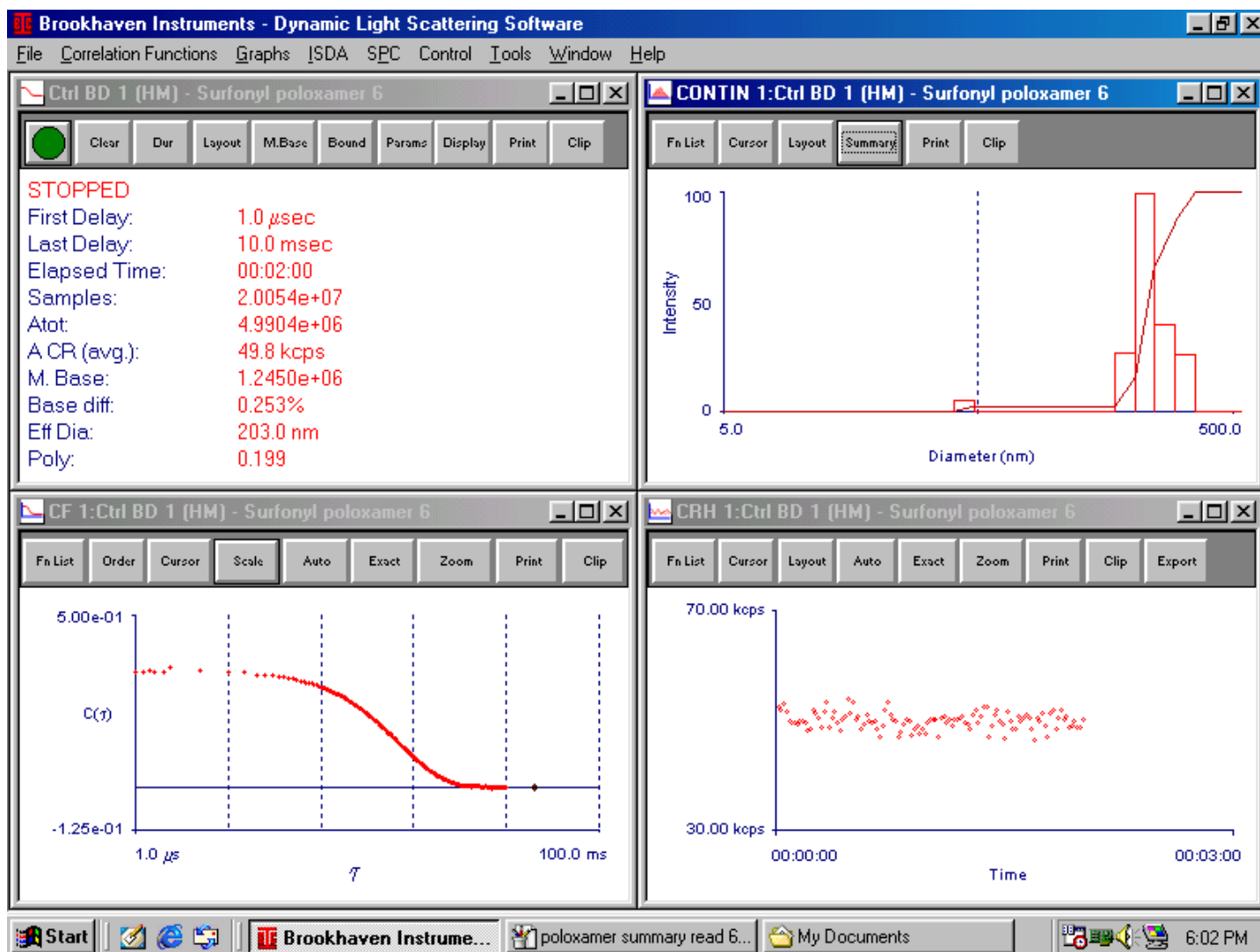


Figure 6 : DLS results of sample 3.

## CONCLUSION

If there are any impurities in the sample we will observe a flat peak, and if there are no impurities in the sample then we will get good peaks. The Nanoparticles size we got is good enough to penetrate in to the chronic wounds but its better to decrease particle size for more effective penetration in to the chronic wounds, so inorder to decrease the nanoparticles size we need to sonicate the prepared nanoemulsion. These nanoparticles should be tested by using small angle x-ray scattering studies and the penetration studies of these nanoparticles will be performed. DLS is rapid, non-invasive technique<sup>[10]</sup> for determination of Nanoparticles size. The sample 1 contains larger nanoparticles (i.e 312.4nm) when compared with that of sample 2 (193.3nm) and sample 3 (204.3nm) because sample 1 contains carbopol which is high molecular weight polymeric compound.

## **ACKNOWLEDGEMENT**

At the end of my thesis I would like to thank all those people who made this thesis possible and an unforgettable experience for me.

First of all, I would like to express my deepest sense of Gratitude to Dr.Patty Fu Giles, who offered this research work.

I would like to thank Dr.Lurio, Rahul Khanke, and Gopala Krishna (NIU) and GSU for the support.

I am thankful to parents and friends for their support, encouragement, and love given to me during the course of this thesis.

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